Chemical Physics Letters 465 (2008) 1–9

Contents lists available at ScienceDirect

Chemical Physics Letters

journal homepage: www.elsevier.com/locate/cplett

FRONTIERS ARTICLE

On the formation of higher carbon oxides in extreme environments

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A R T I C L E   I N F O

Article history:
Received 15 May 2008
In final form 22 July 2008
Available online 29 July 2008

A B S T R A C T

Due to the importance of higher carbon oxides of the general formula CO_x ($x > 2$) in atmospheric chemistry, isotopic enrichment processes, low-temperature ices in the interstellar medium and in the outer solar system, as well as potential implications to high-energy materials, an overview on higher carbon oxides CO_x ($x = 3$–6) is presented. This article reviews recent developments on these transient species. Future challenges and directions of this research field are highlighted.

1. Introduction

In recent years, the interest in carbon oxides of higher complexity than carbon monoxide (CO; $X^1\Sigma^+$) and carbon dioxide (CO_2; $X^1\sum_g^+$) of the generic formula CO_x ($x > 2$) has been fueled by complex reaction mechanisms of carbon oxides with atomic oxygen in the atmospheres of Mars [1–4] and Venus [5]. Here, carbon dioxide represents the major atmospheric constituent [6]. Laboratory studies suggested that the photodissociation of carbon dioxide by solar photons ($\lambda < 2050$ Å) generates a carbon monoxide molecule plus atomic oxygen. Near the threshold, only ground-state $O(^3P)$ atoms are produced; shorter wavelengths supply also electronically excited oxygen atoms $O(^1D)$ [1]. Electronically excited oxygen atoms are thought to be mainly quenched involving a carbon trioxide molecule (CO_3) of a hitherto unknown structure. Once ground-state oxygen atoms $O(^3P)$ and carbon monoxide have formed, it is difficult to recycle carbon dioxide, since the reversed reaction presents a spin-forbidden process.

Besides the quenching of electronically excited oxygen atoms, the carbon trioxide (CO_3) molecule has been implicated as an important transient species in the ^{18}O isotope enrichment of carbon dioxide in the atmospheres of Earth and Mars [7,8]. Computations and laboratory experiments indicate that the ^{18}O enrichment in ozone might be transferable to carbon dioxide [9,10], possibly via a CO_3 intermediate. Due to the potential role of carbon trioxide in atmospheric chemistry, various kinetics and dynamics studies have been carried out to access the CO_3 surface and to determine the temperature-dependent rate constants of the reaction of electronically excited oxygen atoms, $O(^1D)$, with carbon dioxide. At room temperature, rate constants of a few 10^{-10} cm^3 s^{-1} have been derived [11–13]. This order of magnitude suggests that the reaction has no activation energy, proceeds with almost unit efficiency, and most likely involves a reaction intermediate. However, neither reaction products (kinetics studies) nor the nature of the intermediate (kinetics and dynamics studies) were determined. On the other hand, a $CO(X^1\Sigma^+) + O_2(X^3\sum_g^-)$ exit channel was found to have an *activation energy* between 15 and 28 kJ mol^{-1} in the range of 300–2500 K [14]. Atreya et al. pointed out the necessity to incorporate heterogeneous reactions on aerosols or carbon dioxide ice particles in the Martian atmosphere [15–17]. However, these processes have not been investigated in the laboratory so far. Also, the explicit structure of the atmospherically relevant CO_3 intermediate has not been unraveled to date [18,19].

Besides the atmospheric chemistry of Venus, Earth, and Mars and the ^{18}O enrichment processes, solid carbon dioxide presents an important constituent of interstellar ices as present on submicrometer sized grain particles in cold interstellar clouds holding temperatures as low as 10 K. Here, ice mixtures comprising water (H_2O) (100), carbon monoxide (CO) (7–27), methanol (CH_3OH) (<3.4), ammonia (NH_3) (<6), methane (CH_4) (<2), and carbon dioxide (CO_2) (15) were identified unambiguously via infrared spectroscopy towards the dense cloud TMC-1 employing the field star Elias 16 as a black body source; the numbers in parentheses indicate the relative abundances compared to water ice. These clouds interact with ultraviolet photons (<13.2 eV) and energetic particles, predominantly from galactic cosmic rays. Henceforth, pristine ice mantles are processed chemically by the cosmic ray-induced ultraviolet radiation present even in the deep interior of dense clouds [20]. This can lead to the formation of new molecules in the solid state via non-equilibrium (non-thermal) chemistry even at temperatures as low as 10 K. Likewise, carbon dioxide ices have been detected in the outer solar system on Triton and Ganymede (Neptune's and Jupiter's largest moons, respectively). Here, charged particles from the planetary magnetospheres can potentially release oxygen atoms which may react with carbon dioxide to form carbon trioxide and higher carbon oxides.

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doi:10.1016/j.cplett.2008.07.076

Finally, it should be recalled that intensive research has been carried out to develop new high-energy materials (HEMs) to meet needs for future defense and space science applications like novel explosives and rocket propellants [21]. Particular attention has been devoted to cyclic carbon oxides of the generic formula CO_x ($x = 3–6$). These higher-order oxides of the main group IV element carbon are highly energetic and therefore, candidates for high-energy density materials; Shkrob suggested these oxides also as model compounds to study high velocities of detonation (VOD) and to possibly control the energy release from high-energy density material [22].

Due to the importance of higher carbon oxides in atmospheric chemistry, isotopic enrichment processes, low-temperature ices in the interstellar medium and in the outer solar system, as well as potential implications to high-energy materials, this *Frontiers Article* presents a historical overview on higher carbon oxides CO_x ($x = 3–6$) and reviews recent developments on how to synthesize these transient species experimentally and computationally. The final chapter highlights future challenges and directions of this research field.

2. Historical overview

2.1. Carbon trioxide (CO_3) isomers

Experimental and theoretical studies of the properties and formation routes of carbon trioxide isomers started more than four decades ago. In 1966, Ung and Schiff [23] conducted gas phase experiments and photolyzed carbon dioxide under bulk conditions. Based on the kinetics, the mass balance of the detected carbon monoxide (CO) and molecular oxygen (O_2) products, and the reactions of methane (CH_4), molecular hydrogen (H_2), and dinitrogenoxide (N_2O), the authors postulated the presence of a hitherto elusive reactive species, carbon trioxide (CO_3), in the gas phase. However, an explicit detection of this unstable molecule failed; further, the authors did not recommend any structure of the carbon trioxide molecule.

In the same year, Moll et al. [24] identified a C_{2v} symmetric carbon trioxide molecule (CO_3) in carbon dioxide and carbon dioxide-ozone matrices at temperatures as low as 50 K (Fig. 1). Combining these data with Jacox and Milligan studies [25], both groups assigned four fundamentals at 2045 cm^{-1} (C=O stretch), 1073 cm^{-1} (O–O stretch), 972 cm^{-1} (C–O stretch), 593 cm^{-1} (C–O stretch), and 568 cm^{-1} (O–C=O) in low-temperature matrices; in argon matrices, these absorptions were shifted to 2053, 1070, 975, and 564 cm^{-1} [26]; no feature around 593 cm^{-1} was identified in solid argon. Absorptions at 1894 cm^{-1} (argon matrix) and 1880 cm^{-1} (carbon dioxide matrix) were tentatively assigned as a Fermi resonance of the 2045 cm^{-1} band with an overtone of the 972 cm^{-1} fundamental. These results suggested that photolysis and radio frequency discharges of ozone and carbon dioxide generate atomic oxygen; at that time, the spin states of the liberated oxygen atom were not assigned. Based on the observed infrared frequencies and isotope substitution pattern, a planar, C_{2v} symmetric structure was derived in which the carbon atom is bound by a strong, exocyclic carbonyl bond to one oxygen atom, and by weaker bonds to two oxygen atoms placed overall in a cyclic geometry. These experiments presented explicit evidence that, a cyclic carbon trioxide molecule (CO_3) is stable in low-temperature matrices. In addition to this identification, the results of photolysis of ^{18}O enriched carbon dioxide samples led to the hypothesis that, besides the C_{2v} isomer, a D_{3h} or C_{3v} symmetric carbon trioxide molecule, in which all oxygen atoms are equivalent, should also exist as a reactive, not-isolatable intermediate to form the C_{2v} symmetric structure. Finally, the authors provided compelling evidence that the decomposition of carbon trioxide molecules leads to carbon dioxide molecules and atomic oxygen. Shortly after this study, Weissberger et al. carried out photolysis experiments of solid carbon dioxide matrices and of mixtures of ozone and carbon dioxide dispersed in solid argon. These experiments strongly indicated that an electronically excited oxygen atom ($O(^1D)$) can react with carbon dioxide to actually synthesize the C_{2v} symmetric carbon trioxide isomer [26]. An early review on carbon trioxide concluded that further studies are necessary to elucidate the structure and the electronic configuration of this transient species [27].

The subsequent years elucidated the electronic structures of the carbon trioxide molecule(s). Applying Hueckel molecular orbital theory, correlation diagrams, and Walsh rules, Gimarc and Chou predicted that the molecule favors a planar, C_{2v} symmetric structure [28]. Calculations predicted that this molecule is metastable toward dissociation into carbon monoxide (CO) and electronically excited molecular oxygen (O_2; $a^1\Delta_g$); an alternative decomposition pathway could involve linear carbon dioxide (CO_2) and electronically excited oxygen atoms ($O(^1D)$). The latter mechanism was also verified in photolysis experiments of ozone in carbon dioxide [29]. Olsen and coworkers [30] applied the extended Hueckel and intermediate neglect of differential overlap (INDO) methods to investigate various molecular geometries of the carbon trioxide molecule in its pyramidal (C_{3v}) and symmetric trigonal C_{2v} shaped structures. Both methods predicted the C_{2v} shaped structure holding a X^1A_1 electronic ground-state to be favorable in energy. The authors also suggested that the closed shell $^1A_1$ ground-state correlates with the $^1E'$ wave function in D_{3h} symmetry; consequently, the adoption of the C_{2v} symmetry of carbon trioxide can be attributed to the Jahn–Teller effect. Subsequent calculations [31,32] correlated with the previous results favoring a C_{2v} symmetric structure of the molecule. The short carbon–oxygen bond distance of the exocyclic unit of only 126.5 pm indicated a carbonyl group; likewise, the extended carbon–oxygen bonds of 147.3 pm as found in the ring suggest the existence of carbon–oxygen single bonds. Finally, the oxygen–carbon–oxygen angle was derived to be about 66°. This geometry was also verified in subsequent matrix studies by Jacox and Milligan [25]. Finally, high pressure kinetics studies of the gas phase reaction of electronically excited oxygen atoms ($O(^1D)$) have been conducted [33]. The authors inferred the formation of transient carbon trioxide molecules with lifetimes in the order of 1–10 ps. The dominant process was suggested to be quenching of $O(^1D)–O(^3P)$, which proceeded via the CO_3^* intermediate. However, no structure of the carbon trioxide molecule was proposed. In strong contrast to previous assignments, LaBonville et al. suggested a C_s-symmetric structure of the carbon trioxide molecule [34].

After a decade, the interest in the carbon trioxide system resumed, predominantly due to the development of the novel electronic structure methods [35]. Pople et al. tackled the energies and electron configuration of open and closed-shell carbon trioxide molecules utilizing ab initio molecular orbital calculations. At the highest level of theory used (MP2/6-31G*), including the effect of electron correlation, the cyclic, C_{2v} symmetric structure was found to be more stable by 230 kJ mol^{-1} than any open shell electron configuration; this result was in agreement with a subsequent study by Francisco et al. [36]. The authors also emphasized that this molecule is only metastable by approximately 17 kJ mol^{-1} with respect to ground-state oxygen atoms ($O(^3P)$) and linear carbon dioxide. Also, the dissociation energy to form carbon dioxide plus electronically excited oxygen atoms ($O(^1D)$) was found to be very low (75 kJ mol^{-1}). Steinfatt postulated that the decay of the cyclic carbon trioxide molecule is also correlated with strong chemiluminescence signals observed in the perhydrolysis of phosgene in presence of organic sensitizers [37].

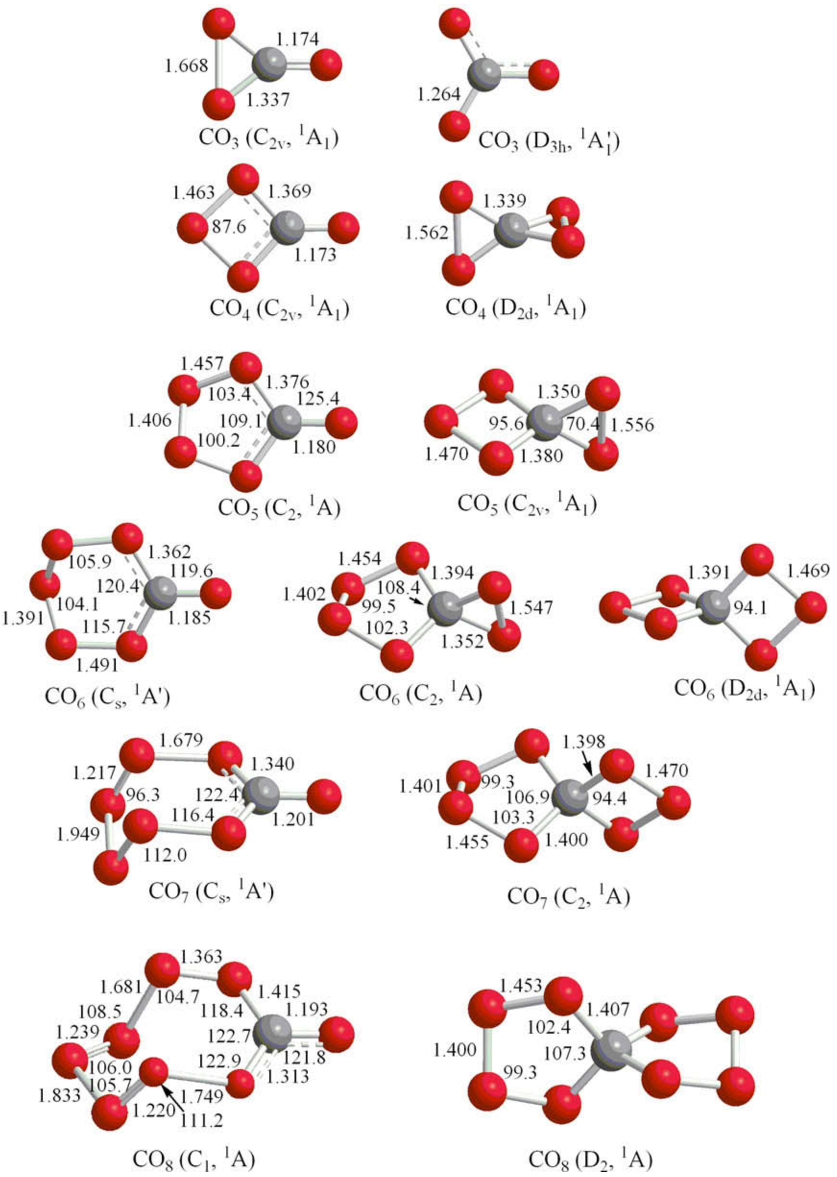

Fig. 1. Optimized geometries of various isomers of the CO_x molecules ($x = 3$–8). Bond lengths are given in Å and bond angles in degrees. Symmetries and ground-state electronic terms are also provided.

Ongoing improvements in computational methods pushed the research on the carbon trioxide system to the next level. Van de Guchte et al. [38] conducted a systematic ab initio study of D_{3h} and C_{2v} symmetric structures. The authors concluded that the optimized structure in C_{2v} symmetry (at the SCF level) is higher in energy than the optimum structure in D_{3h} symmetry. However, Castro and coworkers utilized a more sophisticated approach [39]. They performed many-body perturbation theory and coupled-cluster calculations on the carbon trioxide molecule in D_{3h} and C_{2v} symmetries. The relative energy location of the $^1A_1$ (C_{2v}) and $^1A_1'$ (D_{3h}) closed-shell states is found to be extremely sensitive to electron-correlation corrections. At the highest level of theory, the $^1A_1$ (C_{2v}) state was found to be below the $^1A_1$ (D_{3h}) state by about 18 kJ mol^{-1}. This study showed that actually two metastable carbon trioxide isomers can exist, and that the cyclic structure is more stable compared to the D_{3h} isomer. This conclusion was confirmed by a consecutive investigation of this system [40]. Froese et al. also studied for the first time the corresponding triplet surface which lies at least 251 kJ mol^{-1} above the lowest closed-shell singlet molecule.

Interest resumed on the carbon trioxide system to tackle the C_{2v} and D_{3h} symmetric carbon trioxide isomers. Markovits et al. demonstrated computationally that a carbon trioxide molecule bound to a Pt(1 1 1) surface depicts a similar equilibrium geometry than the carbonate ion (CO_3^{2-}). In addition to the well-known infrared spectrum of the cyclic carbon trioxide molecule, Abreu et al. [41] provided a computed Raman spectrum. Supporting a previous computational study [39], the Raman spectrum was found to show a very sensitive dependence to the treatment of electron correlation. Triggered by its potential relevance to atmospheric chemistry, further computations probed the electron affinity of both C_{2v} and D_{3h} structures. Here, electron affinities of 3.85–4.08 eV were recommended to yield in both cases the acyclic CO_3^- anion [42]. The latest theoretical study [43] investigated the electronic structure of carbon trioxide and vibronic interactions involving Jahn–Teller states. The authors concluded that ground-state equilibrium structures and frequencies are strongly affected by vibronic interactions with low-lying excited states. For example, at the D_{3h} geometry, the vibronic interactions are enhanced by the Jahn–Teller character of the excited states and the complete theoretical description of this molecule might require going beyond harmonic description within the adiabatic approximation.

In summary, previous studies demonstrated experimentally the existence of the cyclic, C_{2v} symmetric carbon trioxide molecule in low-temperature matrices and as a transient species in the photodissociation of carbon dioxide containing gas mixtures. The second isomer, the D_{3h} symmetric isomer, was proposed theoretically to exist, but it is higher in energy than the cyclic molecule by about 18 kJ mol^{-1}. According to calculations, both structures are connected via a transition state located 36 kJ mol^{-1} above the cyclic molecule [44]. Evidence for an interconversion of both structures first came when Baulch and Breckenridge, using isotopic labeling, found that an attacking oxygen atom has an approximately statistical chance of being incorporated into the carbon dioxide molecule [45].

2.2. Carbon tetraoxide (CO_4) isomers

Studies on the carbon tetraoxide molecule (CO_4) have been restricted to theoretical investigations. More than a decade ago, Averyanov et al. predicted the existence of a metastable carbon tetraoxide molecule [46]. Based on electronic structure calculations, the authors inferred a spirane-like, D_{2d} symmetric structure with a X^1A_1 electronic ground-state (Fig. 1). Applying selection rules for chemical reactions, this molecule was postulated to decay either to a ground-state, C_{2v} symmetric carbon trioxide molecule (CO_3; X^1A_1) (Fig. 1) plus electronically excited atomic oxygen ($O(^1D)$) or alternatively to a linear carbon dioxide molecule (CO_2; $X^1\sum_g^+$) together with electronically excited molecular oxygen (O_2; $a^1\Delta_g$); note that the latter route had to proceed via a cyclic carbon dioxide intermediate (CO_2; X^1A_1) which had to ring-open to the linear carbon dioxide molecule. Subsequent studies by Averyanov et al. expanded preliminary computational investigations and explored the global CO_4 potential energy surface at the SCF, MP2, MP4, and CISD levels of theory using the 6-31G* basis set [47,48]. These refined computations located two local minima: the previously assigned D_{2d} symmetric isomer and a newly discovered C_{2v} symmetric isomer. These investigations postulated that, both structures are vibrationally stable, but metastable with respect to the formation of carbon dioxide (CO_2; $X^1\sum_g^+$) plus electronically excited molecular oxygen (O_2; $a^1\Delta_g$). The C_{2v} symmetric structure was found to be lower in energy by about 134 kJ mol^{-1}. The existence of the energetic D_{2d} symmetric isomer was confirmed by Song and coworkers exploiting second-order Moller-Plesset (MP2) and a quadratic configuration interaction (CI) through single and double excitation (QCISD) calculations using 6-31G(d) and 6-311G(d,p) basis sets [49]. These computations labeled CO_4 (D_{2d}) as a potential high-energy oxidizer.

2.3. Carbon pentaoxide (CO_5) and carbon hexaoxide (CO_6) isomers

Computational studies on carbon pentaoxides and carbon hexaoxides are sparse. As a matter of fact, only a single theoretical investigation was conducted [50]. Elliott et al. predicted the existence of two isomeric pairs. For the CO_5 isomers, these are C_2 and C_{2v} symmetric structures where the central carbon atom is connected to a carbonyl group and an O_4 ring (C_2) as well as a bi-cyclic molecule holding a CO_3 and a CO_4 ring (C_{2v}). The latter molecule was predicted to be less stable by 166 kJ mol^{-1} compared to the C_2 isomer. In case of the CO_6 system, the authors identified a C_2 and D_{2d} symmetric structure; here, the C_2 isomer is more stable by 59 kJ mol^{-1} compared to the D_{2d} symmetric molecule. The most stable structure is formally derived from a CO_4 ring merged with a CO_2 ring via the central carbon atom. The D_{2d} symmetric isomer has two CO_3 cycles. Surprisingly, no CO_5 or CO_6 isomers were identified which have a carbonyl group as the C_{2v} symmetric CO_3 and CO_4 molecules.

3. Present status of the field

The overview recapitulated that among the higher carbon oxides CO_x ($x = 3$–6), only the C_{2v} symmetric CO_3 (X^1A_1) has been detected experimentally in low-temperature matrices. Computational studies predicted further that at least a second, D_{3h} symmetric CO_3 should exist. Likewise, higher carbon oxides ranging from CO_4 to CO_6 are expected to be metastable and possibly detectable experimentally. Low-temperature spectroscopy combined with a computational study of the structures, energetics, and infrared spectroscopic properties of the higher carbon oxides presents a powerful tool to identify these molecules in icy matrices. Here, the electronic structure calculations serve as a 'guide' to search for the transitions of higher carbon oxides in the chemically relevant, mid infrared regime of 5000–400 cm^{-1}. But how can these molecules be 'made' in the laboratory? Previous laboratory studies, aimed to investigate the interaction of ionizing radiation with astrophysically relevant low-temperature ices, showed that the energy transfer from energetic electrons (keV range) penetrating thin ice layers of a few 100 nm to the surrounding molecules can lead to a unimolecular decomposition of the target molecules forming reactive radicals and atoms [51]. An interaction of solid nitrogen molecules embedded in low-temperature (10 K) matrices, for example, with keV electrons generates suprathermal nitrogen atoms [52]. These atoms hold access kinetic energies up to a few eV and therefore, are not in thermal equilibrium with the surrounding matrix. These 'suprathermal atoms' can react with molecules of the surrounding ice matrix. For instance, the linear $N_3(X^2\Pi)$ radical (nitrogen ices) [52] and the C_s symmetric $OCNO(X^2A'')$ [53] intermediate can be synthesised via the reaction of a single suprathermal nitrogen atom with one nitrogen and carbon dioxide molecule, respectively. Likewise, a unimolecular decomposition of molecular oxygen [54] and carbon dioxide [53] leads to the formation of two oxygen atoms as well as carbon monoxide plus atomic oxygen, respectively. Based on these considerations, we expect that a processing of low-temperature carbon dioxide matrices by energetic (keV) electrons will lead to the generation of energetic, suprathermal oxygen atoms which can react then with the surrounding carbon dioxide matrix to potentially synthesize higher carbon oxides. However, it should be stressed, that compared to a photodissociation of molecules in the gas phase, which may generate atoms in selected electronic states (for example the photodissociation of ozone (O_3) at 248 nm leads to electronically excited oxygen atoms $O(^1D)$, the interaction of energetic electrons with molecules in ices can generate both ground-state $O(^3P)$ and electronically excited oxygen atoms $O(^1D)$. Therefore, it may be difficult to extract the actual reaction mechanisms leading to the synthesis of higher carbon oxides in low-temperature carbon dioxide matrices. Nevertheless, recall that the first and foremost goal is to actually *synthesize* new carbon oxides in the laboratory and to *identify* the nature of the isomer(s) formed spectroscopically via infrared spectroscopy at 10 K. Secondly, by following the development of the infrared absorption features in real time during the irradiation exposure on line and in situ, it will be also feasible to extract information on the kinetics and reaction mechanisms how the higher carbon oxides form. Finally, the laboratory experiments can also help to elucidate the stability of the newly formed molecules in the ices. By increasing the temperature of the carbon dioxide ice matrix in the post-irradiation phase and monitoring the decay of the infrared absorptions of the higher carbon oxides, it is feasible to extract information on the stability and decomposition temperature of these molecules.

3.1. Electronic structure calculations

Electronic structure calculations and the derived infrared spectra together with their intensities in particular present valuable tools to predict the geometries of – if they exist – multiple isomers and the position of the vibrational fundamentals of the newly formed molecules. The optimized geometries of various CO_x isomers ($x = 3$–8) are illustrated in Fig. 1 and their symmetries, ground electronic state terms, and relative energies with respect to the most stable structures for each molecule are collected in Table 1.

The most detailed calculations of the potential energy surface have been performed for the CO_3 species [55], for which geometry optimization and vibrational frequency calculations were carried out at the multireference CASSCF level of theory with the active space including 16 electrons distributed on 13 orbitals (i.e., the complete valence active space excluding 2s orbitals of oxygen atoms) and the 6-311G* basis set. Single-point energies of various isomers and transition states were refined using the coupled-clusters CCSD(T) and multireference configuration interaction MRCI(16,13) methods with the 6-311+G(3df) basis set. The calculations have confirmed that the cyclic C_{2v} CO_3 isomer is the most stable, but the acyclic D_{3h} structure is only slightly higher in energy, by 13.8 and 0.4 kJ mol^{-1} at the CCSD(T)/6-311+G(3df) and MRCI/6-311+G(3df) levels of theory, respectively. The two isomers are separated by a barrier of 25 kJ mol^{-1} according to supposedly most accurate MRCI calculations. The C_{2v} isomer resides 197.5 kJ mol^{-1} below $O(^1D)+CO_2$ but is nearly isoenergic with $O(^3P)+CO_2$. However, the fragmentation of CO_3 to $O(^3P)+CO_2$ is spin-forbidden and can occur via the minimum energy structure on the singlet-triplet seam of crossing lying 146.4 kJ mol^{-1} above the C_{2v} CO_3 isomer. Dissociation to $O_2(X^3\sum_g^-) + CO$ is also spin-forbidden and endothermic by 48 kJ mol^{-1}. Hence, we can conclude that CO_3 should be a rather stable molecule, which can be produced in the exothermic $O(^1D)+CO_2$ reaction.

For the higher carbon oxides (CO_x, $x > 3$), our discussion is based on B3LYP/6-311G(d) and B3LYP/6-311+G(d) optimized geometries and CCSD(T)/6-311+G(d) relative energies of different isomers with zero-point vibrational energy corrections taken from the B3LYP calculations. At the B3LYP level, the influence of the inclusion of diffuse functions in the basis set appeared to be insignificant. Elliot and Boldyrev [50] have also shown that the differences in geometric parameters of CO_x optimized at the B3LYP, CASSCF(8,8), and CCSD(T) levels are rather minor, especially between B3LYP and the most accurate CCSD(T) calculations.

Table 1
Calculated symmetry, ground electronic state terms, and relative energies of isomers (E_{rel}) of the CO_x molecules ($x = 3$–8)[g]

Molecule	Isomer, symmetry	Electronic state	E_{rel} (kJ mol^{-1})
CO_3	$O_2C{=}O$, C_{2v}	$^1A_1$	0.0
	$OC(O)O$, D_{3h}	$^1A_1'$	13.8[a], 0.4[b]
CO_4	$O_3C{=}O$, C_{2v}	$^1A_1$	0.0
	O_2CO_2, D_{2d}	$^1A_1$	137.7[c]
CO_5	$O_4C{=}O$, C_2	^1A	0.0
	O_3CO_2, C_{2v}	$^1A_1$	166.1[c]
CO_6	$O_5C{=}O$, C_s	$^1A'$	0.0
	O_4CO_2, C_2	^1A	112.9[d]
	O_3CO_3, D_{2d}	$^1A_1$	173.4[d]
CO_7	$O_6C{=}O$, C_s	$^1A'$	0.0
	O_4CO_3, C_2	^1A	203.6[e]
CO_8	$O_7C{=}O$, C_1	^1A	0.0
	O_4CO_4, D_2	^1A	106.2[f]

[a] Calculated at the CCSD(T)/6-311+G(3df) level in Ref. [55].

[b] Calculated at the MRCI+Q(16,13)/6-311+G(3df) level in Ref. [55].

[c] From CCSD(T)/6-311+G* calculations in Ref. [50].

[d] Based on the present CCSD(T)/6-311+G* calculations for the C_s structure and similar calculations for the C_2 and D_{2d} isomers in Ref. [50].

[e] Based on the present CCSD(T)/6-311+G* calculations for the C_s structure and similar calculations for the C_2 isomer in Ref. [50].

[f] Based on the present CCSD(T)/6-311+G* calculations for the C_1 structure and similar calculations for the D_2 isomer in Ref. [50].

[g] The ab initio calculations produce zero temperature results. Thermal corrections to the relative energies of isomers are normally very small and are not expected to change relative energies of different isomers by more than 1 kJ mol^{-1}.

Two isomers have been found for the CO_4 species. The C_{2v} structure ($O_3C{=}O$) includes the carbonyl $C{=}O$ group merged with the diamond-shaped CO_3 ring via the central carbon atom. The D_{2d} isomer (O_2CO_2) is spirane-like and is made from two three-member CO_2 rings located in perpendicular planes. According to the CCSD(T)/6-311+G(d) calculations, [50] the C_{2v} structure is significantly, by 137.7 kJ mol^{-1}, more favorable than D_{2d}. Next, the structures of higher CO_x molecules can be derived from CO_4 isomers by expansion of the CO_3 and CO_2 rings through the addition of extra oxygen atoms. For instance, the expansion of the CO_3 ring in the C_{2v} structure of CO_4, while keeping the carbonyl moiety intact, gives the C_2-symmetric isomer of CO_5. $CO_5(C_2)$ has a non-planar (puckered) CO_4 ring attached to the $C{=}O$ group ($O_4C{=}O$). Alternatively, ring-expansion in the D_{2d} CO_4 isomer produces the C_{2v} structure of CO_5 with the merged CO_3 and CO_2 rings in perpendicular planes (O_3CO_2). As for CO_4, the C_2 isomer containing the carbonyl group is much more stable than the C_{2v} form; the energy difference is as high as 166.1 kJ mol^{-1}. Elliott and Boldyrev [50] considered only two forms of CO_6, C_2 and D_{2d}, both obtained by ring expansions of the least-stable C_{2v} isomer of CO_5. In particular, the C_2 structure of CO_6 is made by expansion of the diamond-shaped CO_3 ring to the puckered CO_4 cycle, whereas the D_{2d} CO_6 isomer is produced by expansion of the CO_2 triangle to the CO_3 diamond. Meanwhile, the expansion of the CO_4 ring in the most stable C_2 isomer of CO_5, which was not considered earlier, gives a C_s structure of CO_6 combining the carbonyl group with a non-planar CO_5 cycle. According to our CCSD(T)/6-311+G(d) calculations, the C_s-symmetric $O_5C{=}O$ isomer represents the lowest in energy CO_6 form; it is calculated to be more favorable than the C_2 (O_4CO_2) and D_{2d} (O_3CO_3) isomers by 112.9 and 173.4 kJ mol^{-1}, respectively.

Elliott and Boldyrev [50] calculated only one isomer each for CO_7 and CO_8, C_2-symmetric O_4CO_3 and D_2-symmetric O_4CO_4, both made by expansion of the CO_2 triangle in the C_2-symmetric CO_6 structure O_4CO_2 first to CO_3 and then to CO_4 rings. However, since the isomers containing the carbonyl fragment are the most stable structures of CO_x with $x = 3$–6, we searched for a possibility of a further ring expansion in the C_s-symmetric CO_6, $O_5C{=}O$, while maintaining the $C{=}O$ group untouched. The geometry optimization gave new isomers of CO_7 and CO_8, $O_6C{=}O$ of C_s symmetry and non-symmetric $O_7C{=}O$. At the CCSD(T)/6-311+G(d) level, $O_6C{=}O$ appeared to be 203.6 kJ mol^{-1} more stable than O_4CO_3, whereas $O_7C{=}O$ lies 106.2 kJ mol^{-1} lower in energy than O_4CO_4. Summarizing, we can conclude that the $O_{x-1}C{=}O$ isomers containing the carbonyl group are the most stable forms CO_x and they are 100–200 kJ mol^{-1} more favorable than the other bi-cyclic $O_{x-n}CO_n$ ($n > 1$) structures.

As seen in Fig. 1, the $C{=}O$ bond length in the $O_{x-1}C{=}O$ structures gradually increases from 1.174 and 1.173 Å in CO_3 and CO_4 to 1.180, 1.185, and 1.201 Å in CO_5, CO_6, and CO_7, respectively, but then slightly decreases to 1.193 Å in CO_8. The single C–O bonds are found to be the shortest in the three-member CO_2 rings, 1.337–1.352 Å, and are longer in CO_3 and CO_4 cycles, 1.369–1.398 and 1.376–1.407 Å, respectively. In the larger rings, the calculated C–O distances change non-monotonically, from 1.362 Å in CO_5 to 1.340 Å in CO_6, but then to 1.313 and 1.415 Å in CO_7. On the other hand, the O–O distances vary in a much wider range, 1.547–1.668 Å in three-member CO_2 cycles, 1.463–1.470 Å in CO_3 diamonds, 1.400–1.457 Å in CO_4 rings, and 1.391–1.491 Å in CO_5. Finally, in the CO_6 and CO_7 rings of CO_7 and CO_8 we find bonding

O–O distances as short as 1.217 Å and as long as 1.949 Å, indicating that a usual valence-bond consideration can hardly be applied to these exotic structures.

Vibrational frequencies and infrared intensities for various CO_x isomers discussed in the subsequent section have been calculated at the B3LYP/6-311G* level of theory (except for CO_3, where the CASSCF(16,13)/6-311G* method was used) within harmonic approximation. It should be emphasized that the harmonic approximation almost always overestimates experimental frequencies [56]. An useful approach widely utilized to correct this deficiency is given by scaling procedures [57]; since calculated harmonic frequencies are generally larger than the observed fundamental frequencies, the calculated values are scaled (multiplied) by a *scaling factor*. The scaling factors are not only intended to account for anharmonicity effects that are neglected in the theoretical calculations, but also for an inadequate description of electron correlation, and the use of finite basis sets. For the B3LYP/6-311G* level of theory, a recommended value for this scaling factor is given as 0.9619; based on comparison of the vibrational frequencies from 125 different molecules [58]. Note that the scaled frequencies are essentially computed for the gas phase. In addition matrix effects can shift these fundamentals by a few wavenumbers; typically, in non-polar matrices such as carbon dioxide, these shifts should not be higher than a few wavenumbers [59]. For more accurate determination of a scaling factor for a particular subset of molecules (e.g. CO_x species) it is often desirable to re-calculate a scaling factor based on bands solely arising from similar molecules. The scaling factors that are used here were calibrated for each particular system and were found to be in the range 0.967–0.992, i.e. slightly closer to 1 than the recommended value.

3.2. Low-temperature spectroscopy

3.2.1. Carbon trioxide $CO_3(C_{2v})$

The electron irradiation of the carbon dioxide target leads to rapidly developing new absorption features of carbon monoxide at 2139 cm^{-1} (ν_1, CO stretching) [60]. These findings suggest that the carbon dioxide molecule undergoes unimolecular decomposition to form carbon monoxide plus oxygen atoms. In addition, two absorptions of the ozone molecule were monitored at 1042 cm^{-1} (ν_3, anti symmetric stretch) and the weaker bending mode at 704 cm^{-1} (ν_2) [61]. A quantitative fit of the temporal evolution of the ozone profile suggests that two oxygen atoms combine to form molecular oxygen; the later reacts with a third oxygen atom to synthesize ozone. Besides the carbon monoxide and ozone molecules, four fundamentals of the well-known C_{2v} symmetric cyclic CO_3 structure were identified at 2045 cm^{-1} (ν_1), 1068 cm^{-1} (ν_2), 973 cm^{-1} (ν_5), and 565 cm^{-1} (ν_6). Although the unobserved ν_3 and ν_4 modes have larger absorption coefficients than the detected ν_6 transition, the ν_4 absorption overlaps with the broad ν_2 band of the carbon dioxide reactant; the ν_3 band of carbon trioxide is too close to the cut-off of the detector of the infrared spectrometer to be observable. Finally, we detected also a transition at 1879 cm^{-1}, which was assigned tentatively as a Fermi resonance of the 2044 cm^{-1} band with an overtone of the 973 cm^{-1} fundamental. These experiments act as control experiments and showed explicitly the formation of free oxygen atoms in the irradiated carbon dioxide matrices and the capability of the oxygen atoms to react with carbon dioxide to form the observed C_{2v} symmetric $CO_3(X^1A_1)$ molecule. It should be stressed that the $CO_3(X^1A_1)$ isomer was found to be stable at 10 K, but started to decompose at about 90 K. Finally, at these low irradiation currents, which exposed the sample to a total of 1.0×10^{15} electrons cm^{-2}, no infrared absorptions of hitherto elusive higher carbon oxides could be detected. Therefore, successive experiments exposed the carbon dioxide sample to higher electron fluxes (1.0×10^{16} electrons cm^{-2}); this is expected to significantly zenhance the concentration of suprathermal oxygen atoms formed and could trigger the formation of higher-order carbon oxides.

3.2.2. Carbon trioxide $CO_3(D_{3h})$

An enhanced electron exposure of the carbon dioxide target lead to the observation of the novel $CO_3(D_{3h})$ molecule via infrared spectroscopy. Here, the $CO_3(D_{3h})$ molecule was identified by an absorption centered at 1165 cm^{-1} corresponding to the degenerate ν_1/ν_2 vibrational modes. This band position matches nicely the calculated position of 1168 cm^{-1} after being scaled [62]. This correction is necessary to account for the anharmonicity of the vibrations, which are computed within the harmonic approximation. The observation of the $^{12}C^{18}O_3$, $^{13}C^{16}O_3$, $^{13}C^{18}O_3$, $^{16}O^{12}C^{18}O_2$, and $^{18}O^{12}C^{16}O_2$ isotopomers of this acyclic isomer confirms the assignments. Here, in the $^{12}C^{18}O_2$ system, the ν_1/ν_2 bands were red-shifted to 1152 cm^{-1}. Considering the $^{13}C^{16}O_2$ irradiation experiment, the ν_1 and ν_2 bands of the $^{13}C^{16}O_3$ molecule were found at 1141 cm^{-1}, which agrees nicely with the calculated wavenumber of 1139 cm^{-1}. Also, in the $^{13}C^{18}O_2$ irradiation experiment, the $^{13}C^{18}O_3$ molecule was monitored via an absorption at 1121 cm^{-1} compared to the computed and scaled position of 1126 cm^{-1}. Most importantly, in $^{12}C^{16}O_2/^{12}C^{18}O_2$ ice mixture, *four* acyclic isotopomers were formed: $^{12}C^{16}O_3$, $^{18}O^{12}C^{16}O_2$, $^{16}O^{12}C^{18}O_2$, and $^{12}C^{18}O_3$. Here, the overlapping ν_1 and ν_2 modes resulted in a broad peak centered at 1158 cm^{-1} that had to be deconvoluted. Also, the substitution of one or two oxygen atoms in $^{12}C^{16}O_3$ by ^{18}O reduces the symmetry from D_{3h} to C_{2v}. This eliminates the degeneracy of the ν_1 and ν_2 modes. Summarized, eight isotopomers of the acyclic CO_3 isomer were monitored in low-temperature carbon dioxide samples by comparing the experimentally observed peak positions with the computed, scaled data.

3.2.3. Carbon tetraoxide $CO_4(C_{2v})$

As the irradiation time increased further, additional absorptions appeared in the infrared spectra. These could not be assigned to any CO_3 isomer. Likewise, less intense fundamentals, overtones, and/or combination bands of ozone and carbon monoxide could be ruled out. In the $^{12}C^{16}O_2$ irradiation experiment, the ν_1 vibration of $^{12}C^{16}O_4(C_{2v})$ was observed at 1941 cm^{-1} compared to a calculated wavenumber of 1936 cm^{-1} [63]. The next most intense absorption of the carbon tetraoxide molecule would be the ν_5 vibration centered at 1114 cm^{-1}. However, no absorption could be identified in this region due to its low intensity. Therefore, a confirmation of the assignment of the $CO_4(C_{2v})$ molecule requires an agreement with the predicted isotope shifts in the ν_1 position. In the $^{12}C^{18}O_2$ experiment, $^{12}C^{18}O_4$ was observed at 1908 cm^{-1} which compared well to a scaled value of 1899 cm^{-1}. In the $^{13}C^{16}O_2$ experiment, $^{13}C^{16}O_4$ was observed at 1894 cm^{-1} which agrees with the theoretical value of 1886 cm^{-1}. Lastly, in the $^{13}C^{18}O_2$ irradiation experiment $^{13}C^{18}O_4$ was observed at 1855 cm^{-1} compared to the scaled theoretical shift of 1847 cm^{-1}. The consistent agreement of the peak positions of the ν_1 fundamental vibrations of the $CO_4(C_{2v})$ isotopologues with the theoretically predicted shifts confirmed the assignment of the carbon tetraoxide molecule. The assignment of the hitherto elusive D_{2d} symmetric $CO_4(D_{2d})$ isomer still awaits confirmation. How stable is this newly observed $CO_4(C_{2v})$ molecule? After the irradiation, the ice was left isothermal at 10 K. There was no observable change in the column density of carbon tetraoxide (C_{2v}) indicating that the product was stable and that there were no residual reactions occurring in the ice to form $CO_4(C_{2v})$. The ice was then heated to further check the stability of the carbon tetraoxide molecule. In the infrared spectra carbon tetraoxide absorptions remained until about 120 K. This high-temperature is interesting because $CO_4(C_{2v})$

should be unstable with respect to dissociation to $CO_2(X^1\sum_g^+) + O_2(X^3\sum_g^+)$ [48]. However, Averyanov et al. predicted a significant barrier for this spin-forbidden process. A barrier is also likely to be present in the spin-allowed dissociation to $CO_2(X^1\sum_g^+) + O_2(a^1\Delta_g)$.

3.2.4. Carbon pentaoxide $CO_5(C_2)$

During the irradiation of the $^{12}C^{16}O_2$ target, the ν_1 vibration of $^{12}C^{16}O_5(C_2)$ was observed at 1912 cm^{-1} [64], this compares nicely to the calculated wavenumber of 1914 cm^{-1}. Besides the ν_1 vibration, the next most intense absorption of the carbon pentaoxide molecule would be the ν_7 vibration centered at 1092 cm^{-1}. However, no absorption could be identified in this region due to its low intensity. The ν_7 vibration should be almost four times less intense than the ν_1 vibration. Therefore, once again, a confirmation of our assignment of the $CO_5(C_2)$ molecule requires an agreement with the predicted isotope shifts in the ν_1 position. In the $^{12}C^{18}O_2$ experiment, $^{12}C^{18}O_5$ was observed at 1872 cm^{-1} which agrees well with the scaled value of 1876 cm^{-1}. In the $^{13}C^{16}O_2$ study, $^{13}C^{16}O_5$ was monitored at 1873 cm^{-1}; this data is very close to the scaled theoretical value of 1865 cm^{-1}. Lastly, in the $^{13}C^{18}O_2$ irradiation exposure, $^{13}C^{18}O_4$ was observed at 1829 cm^{-1} compared to the scaled theoretical shift of 1826 cm^{-1}. The consistent agreement of the peak positions of the ν_1 fundamental vibrations of the $CO_5(C_2)$ isotopologues with the theoretically predicted shifts confirmed the identification of the C_2-symmetric carbon pentaoxide molecule. To investigate the stability of the $CO_5(C_2)$ molecule, a similar approach to $CO_4(C_{2v})$ was conducted. Here, the $CO_5(C_2)$ isomer was found to be stable at 10 K. Upon warming up the sample, the infrared spectra suggest that the carbon pentaoxide absorptions remained until about 106 K. This temperature is interesting: according to the calculations conducted by Elliot et al. three exoergic dissociation pathways exist. These are the decay to form $CO_2(X^1\sum_g^+) + O_3(X^1A_1)$, $CO(X^1\Sigma^+) + 2\ O_2(X^3\sum_g^-)$, and $CO_3(X^1A_1) + O_2(X^3\sum_g^-)$. Consequently, similar to carbon tetraoxide, the experiments suggest that significant energy barriers are involved to dissociate carbon pentaoxide.

3.2.5. Carbon hexaoxide $CO_6(C_s)$

As the irradiation exposure of the $^{12}C^{16}O_2$ sample increased, the ν_1 vibration of the C_s-symmetric $^{12}C^{16}O_6$ isomers was observed at 1876 cm^{-1} compared to a scaled, calculated wavenumber of 1877 cm^{-1} [65]. The next most intense absorption of the carbon hexaoxide molecule is the A'' symmetric vibration, which should be less than half the intensity of the ν_1 vibration. Therefore, confirmation of our assignment of the $CO_6(C_s)$ molecule requires an agreement with the predicted isotope shifts in the ν_1 position. In the $^{12}C^{18}O_2$ experiment, $^{12}C^{18}O_6$ was observed at 1837 cm^{-1}; this data is identical to the scaled value of 1837 cm^{-1}. In the $^{13}C^{16}O_2$ experiment, $^{13}C^{16}O_6$ was observed at 1832 cm^{-1} which agrees with the scaled theoretical value of 1831 cm^{-1}. Lastly, in the $^{13}C^{18}O_2$ irradiation experiment $^{13}C^{18}O_6$ was observed at 1791 cm^{-1} compared to the scaled theoretical shift of 1790 cm^{-1}. The coherent conformity of the absorptions of the ν_1 fundamental vibrations of the $CO_6(C_s)$ isotopologues with the theoretically predicted shifts highlighted the assignment of the C_s-symmetric carbon hexaoxide molecule. It should be stressed that neither the C_2-symmetric bicyclic structure, O_2CO_4, nor the D_{2d} symmetric bi-cyclic structure, O_3CO_3, could be detected. Similar to the $CO_4(C_{2v})$ and $CO_5(C_2)$ molecules, the $CO_6(C_s)$ isomer is stable at 10 K. However, the band region containing the carbon hexaoxide molecule decreased in intensity at around 60 K. This may be an indication of the instability of carbon hexaoxide above 60 K. Here, we see a trend of decreasing stability from about 120 K $CO_4(C_{2v})$ via 106 K $CO_5(C_{2v})$ to 60 K $CO_6(C_s)$ as the numbers of oxygen atoms in the ring grow.

3.3. Formation mechanisms

Besides the identification of four hitherto unknown carbon oxides, i.e. $CO_3(D_{3h})$, $CO_4(C_{2v})$, $CO_5(C_2)$, and $CO_6(C_s)$ based on the infrared features, the studies also followed the temporal evolution of the absorption features in situ. This provided an important chance to quantitate the kinetics of the important reaction pathways of higher carbon oxides in the irradiated carbon dioxide samples. These reactions were not conducted under gas phase single collision conditions, but in a low-temperature carbon dioxide ice (10 K). This makes it sometimes challenging to elucidate the reaction pathways based on the kinetic fits of the temporal profiles of the products observed. In particular, the kinetic studies alone could not provide any evidence to what extend ground-state $O(^3P)$ and/or electronically excited carbon atoms $O(^1D)$ drive the formation of higher carbon oxides. Nevertheless, based on the temporal profiles of the reactant molecules and the products, it was evident that the response of the irradiated carbon dioxide target was dictated by a unimolecular decomposition of carbon dioxide forming carbon monoxide and oxygen atoms (Eq. (1)) via first-order kinetics. The suprathermal oxygen atoms were inferred to react with the carbon dioxide molecules via addition either to the carbon–oxygen double bond forming the cyclic $CO_3(X^1A_1;\ C_{2v})$ molecule (Eq. (2)), but also by addition to the carbon atom of the carbon dioxide molecule yielding the acyclic $CO_3(X^1A_1';\ D_{3h})$ structure. Branching ratios, i.e. the direct ratios of the rate constants of reactions (2) and (3), were determined to be about 7. Therefore, the cyclic structure is, as attributed to statistical and sterical factors, formed preferentially. Note that the authors outlined that the D_{3h} isomer may also be produced by isomerization of the C_{2v} structure and vice versa. However, the kinetic fits were found to be insensitive to both processes meaning that the formation of both CO_3 isomers in the low-temperature samples via reactions (2) and (3) was more important than the isomerization channels. The pathways to synthesize $CO_3(X^1A_1';\ C_{2v})$ and $CO_3(X^1A_1';\ D_{3h})$ have been also confirmed theoretically via electronic structure calculations [60]; both reactions were found to be exoergic (with respect to carbon dioxide and electronically excited oxygen atoms) by 197.5 and 197.1 kJ mol^{-1}, respectively.

$$CO_2(X^1\Sigma_g^+) \rightarrow CO(X^1\Sigma^+) + O(^3P/^1D) \tag{1}$$

$$CO_2(X^1\Sigma_g^+) + O(^3P/^1D) \rightarrow CO_3(X^1A_1; C_{2v}) \tag{2}$$

$$CO_2(X^1\Sigma_g^+) + O(^3P/^1D) \rightarrow CO_3(X^1A_1'; D_{3h}). \tag{3}$$

The kinetics of the higher-order carbonoxides $CO_4(C_{2v})$, $CO_5(C_{2v})$, and $CO_6(C_s)$ could only be rationalized by successive, stepwise reactions of oxygen atoms with the corresponding lower-order carbon oxide (Eqs. (4)–(6)). Here, oxygen atoms reacted with carbon trioxide, CO_3 $(X^1A_1;\ C_{2v})$, to form the C_{2v} symmetric CO_4 isomer via a formal expansion of the cyclic structure by one oxygen atom. Note that in the gas phase, the CO_4 molecule would not be stable; however, the surrounding matrix absorbs the internal energy of the CO_4 isomer via phonon interaction – in a similar manner as for the CO_5 and CO_6 molecules. Stepwise expansions of the ring structure of $CO_4(C_{2v})$ and $CO_5(C_2)$ by one oxygen atom lead to $CO_5(C_2)$ and $CO_6(C_s)$, respectively. It should be stressed that these processes are exoergic by 165.9, 166.3, and 145.2 kJmol^{-1}, respectively, as calculated at the CCSD(T)/6-311+G* level for the reactions of $O(^3P)$ and, correspondingly, by 355.8, 356.1, and 335.1 kJmol^{-1} for the reactions of $O(^1D)$. We would like to discuss briefly the microscopic mechanisms of these reactions. As noted above, Eqs. (4)–(6) can be formally interpreted as stepwise expansions of the ring system by oxygen atoms under conservation of the carbonyl group. Electronically excited oxygen atoms can either insert into an oxygen–oxygen or carbon–oxygen single bond to expand the cyclic structure in one step. Alternatively, electronically excited oxygen might add to the non-bonding pair of a ring-oxygen atom forming a weak, exocyclic oxygen–oxygen bond similar to the bonding scheme present in oxywater (H_2OO) [66]. However, this addition has to be followed by a ring-opening process leading ultimately to a ring expansion by one oxygen atom, but via a two-step mechanism compared to a one-step insertion pathway. The larger cone of acceptance of the cyclic moiety compared to the carbonyl group likely directs the interaction of the oxygen atom with the ring. Electronic structure calculations are currently ongoing to verify these pathways computationally and to expand the knowledge from the CO_3 system to more complex carbon oxides. It should be stressed that related cyclic molecules containing only oxygen atoms such as O_4, O_5, and O_6 are unstable. Therefore, the incorporation of a single carbon atom into the oxygen structure leads to a stabilization of the oxygen ring structure

$$\mathrm{CO_3(C_{2v}) + O(^3P/^1D) \rightarrow CO_4(C_{2v})} \tag{4}$$

$$\mathrm{CO_4(C_{2v}) + O(^3P/^1D) \rightarrow CO_5(C_2)} \tag{5}$$

$$\mathrm{CO_5(C_2) + O(^3P/^1D) \rightarrow CO_6(C_s).} \tag{6}$$

4. Future challenges and directions

The identification of the higher-order carbonoxides $CO_3(D_{3h})$, $CO_4(C_{2v})$, $CO_5(C_{2v})$, and $CO_6(C_s)$ opens up the synthesis of more exotic, oxygen-rich molecules in low-temperature matrices. Here, the $CO_3(C_s)$ isomer (OCOO) and the spirane-type $CO_4(D_{2d})$ molecule are still elusive. Likewise, the stability of the $CO_4(C_{2v})$ and $CO_5(C_{2v})$ molecules beyond the sublimation point of the carbon dioxide matrix could lead to preparation of pure $CO_4(C_{2v})$ and $CO_5(C_{2v})$ ices. Oxygen atoms might be then implanted into these ices to synthesize even higher carbon oxides, possibly CO_7 and CO_8. However, the inherent instability of higher-order oxides as evident from the matrix studies of $CO_4(C_{2v})$ (120 K), $CO_5(C_{2v})$ (106 K), and $CO_6(C_s)$ (60 K) makes this a challenging task. Secondly, it should be stressed that so far all spectroscopic and mechanistic information on higher carbon oxides have been derived from matrix studies. Therefore, future attention should be also directed toward a gas phase preparation of higher carbonoxides. For instance, a co-expansion of ozone–carbon dioxide mixtures in a supersonic beam coupled with a photolysis of the ozone to generate reactive $O(^1D)$ species could yield to vibrationally and rotationally cold carbon trioxide molecules. The latter can be probed then spectroscopically in the gas phase. Likewise, the ionization potentials of the carbon trioxide isomers can be derived utilizing tunable vacuum ultraviolet photons. Finally, the potential energy surfaces of the neutral carbonoxides may be studied utilizing dissociative photodetachment of the corresponding anions like CO_3^- and CO_4^- including transition state spectroscopy to elucidate the role of these carbon oxides in atmospheric and interstellar chemistry.

From the theoretical point of view, more accurate evaluation of fundamental absorptions can be achieved via calculations of anharmonic frequencies. In recent years, various procedures have been developed for anharmonic vibrational calculations, which directly provide fundamental frequencies by computing anharmonic corrections through second-order perturbative [67] or variational methodologies [68]. Although the second-order perturbative approach is somewhat less accurate than the variational method, it is much more computationally efficient but still requires numerical calculations of the third and fourth partial derivatives of energy with respect to molecular coordinates. Such calculations at a reliable theoretical level like CCSD(T) may help to avoid scaling of the calculated frequencies, but they remain challenging because of enormous computing requirements. Second, more detailed studies of the CO_4, CO_5, and CO_6 potential energy surfaces are required in order to characterize kinetic stability of these molecules with respect to various dissociation channels. To attain this goal, one needs to map out not only different CO_x isomers but also transition states for isomerization and fragmentation processes. Additionally, since major dissociation channels involve the production of molecular and/or atomic oxygen in the ground triplet electronic states and are spin-forbidden, one also needs to characterize singlet–triplet conical intersections. Once the singlet and triplet surfaces and their conical intersections are derived from ab initio calculations, it will be possible to apply both adiabatic and non-adiabatic statistical theories, like TST and RRKM, to compute rate constants and branching ratios for the fragmentation of CO_x under various conditions.

Acknowledgements

This project was supported by the Air Force Office of Scientific Research (W911NF-05-1-0448). The work on the D_{3h} symmetric CO_3 isomer was co-sponsored via a Research Assistantship by the National Aeronautics and Space Administration through the NASA Astrobiology Institute (Cooperative Agreement No. NNA04CC08A issued through the Office of Space Science).

References

[1] Y.L. Yung, W.B. DeMore, Photochemistry of Planetary Atmospheres, Oxford University Press, Oxford, 1999.
[2] D.D. Bogard, R.N. Clayton, K. Marti, T. Owen, G. Turner, Space Sci. Rev. 96 (2001) 425.
[3] V.I. Moroz, Adv. Space Res. 22 (1998) 449.
[4] E.M. Galimov, Dok. Akad. Nauk 355 (1997) 382.
[5] M.B. McElroy, J. Geophys. Res. 73 (1968) 1513.
[6] S.K. Atreya, Z.G. Gu, Adv. Space Res. 16 (1995) 57.
[7] A.A. Fedorova, Planet. Space Sci. 50 (2002) 3.
[8] M.H. Thiemens, T.L. Jackson, C.A.M. Brenninkmeijer, Geophys. Res. Lett. 22 (1995) 255.
[9] J. Wen, M.H. Thiemens, J. Geophys. Res. 98 (1993) 12801.
[10] Y.L. Yung, A.Y.T. Lee, J. Geophys. Res. 102 (1997) 10857.
[11] P.H. Wine, A.R. Ravishankara, Chem. Phys. Lett. 77 (1981) 103.
[12] R.A. Young, G. Black, T.G. Slanger, J. Chem. Phys. 49 (1968) 4758.
[13] Available from: <http://kinetics.nist.gov/index.php>.
[14] W. Tsang, R.F. Hampson, J Phys. Chem. Ref. Data 15 (1986) 1087.
[15] A.B. Ivanov, D.O. Muhleman, Icarus 154 (2001) 190.
[16] A. Colaprete, O.B. Toon, J. Geophys. Res. Planets 107 (2002) 5.
[17] R.T. Clancy, B.J. Sandor, Geophys. Res. Lett. 25 (1998) 489.
[18] M.C. Liang, G.A. Blake, B.R. Lewis, Y.L Yung, Yuk L., Proc. Natl. Acad. Sci. USA 104 (2007) 21.
[19] M.J. Perri, A.L. Van Wyngarden, J.J. Lin, Y.T. Lee, K.A. Boering, J. Phys. Chem. A 108 (2004) 7995.
[20] R.I. Kaiser, Chem. Rev. 102 (2002) 1309.
[21] J.P. Agrawal, Prog. Energy Comb. Sci. 24 (1998) 1;
H. Muthurajan, R. Sivabalan, M.B. Talawar, M. Anniyappan, S. Venugopalan, J. Hazardous Mater. 133 (2006) 30;
H. Singh, Explosion 15 (2005) 120;
R.C. Striebich, J. Lawrence, J. Anal. Appl. Pyrol. 70 (2003) 339;
M. Schoenitz, E. Dreizin, J. Propul. Power 20 (2004) 1064.
[22] I.A. Shkrob, J. Phys. Chem. A 106 (2002) 871.
[23] A.Y. Ung, H.I. Schiff, Can. J. Chem. 44 (1966) 1981.
[24] N.G. Moll, D.R. Clutter, W.E. Thompson, J. Chem. Phys. 45 (1966) 4469.
[25] M.E. Jacox, D.E. Milligan, J. Chem. Phys. 54 (1971) 919.
[26] E. Weissberger, W.H. Breckenridge, H. Taube, J. Chem. Phys. 47 (1967) 1764.
[27] K.V. Krishnamurty, J. Chem. Educ. 44 (1967) 594.
[28] B.M. Gimarc, T.S. Chou, J. Chem. Phys. 49 (1968) 4043.
[29] W.B. DeMore, C.W. Jacobsen, J. Phys. Chem. 73 (1969) 2935.
[30] J.F. Olsen, L. Burnelle, Louis, J. Am. Chem. Soc. 91 (1969) 7286.
[31] M. Cornille, J. Horsley, Chem. Phys. Lett. 6 (1970) 373.
[32] J.R. Sabin, H. Kim, Chem. Phys. Lett. 11 (1971) 593.
[33] W.B. DeMore, C. Dede, J. Phys. Chem. 74 (1970) 2621.
[34] P. LaBonville, R. Kugel, J.R. Ferraro, J. Chem. Phys. 67 (1977) 1477.
[35] J.A. Pople, U. Seeger, R. Seeger, P.v.R. Schleyer, J. Comput. Chem. 1 (1980) 199.
[36] J.S. Francisco, I.H. Williams, Chem. Phys. 95 (1985) 373.
[37] M.F.D. Steinfatt, J. Chem. Res. 7 (1984) 211.
[38] W.J. Van de Guchte, J.P. Swart, J.J.C. Mulder, THEOCHEM 37 (1987) 213.
[39] M.A. Castro, S. Sylvio, Chem. Phys. Lett. 177 (1991) 98.

[40] R.D.J. Froese, J.D. Goddard, J. Phys. Chem. 97 (1993) 7484.
[41] E.P. Abreu, M.A. Castro, M.F. Costa, S. Canuto, J. Mol. Spectr. 202 (2000) 281.
[42] C.D. Cappa, M.J. Elrod, Phys. Chem. Chem. Phys. 3 (2001) 2986.
[43] T. Kowalczyk, A.I. Krylov, J. Phys. Chem. A 111 (2007) 8271.
[44] A.S. Averyanov, Y.G. Khait, Y.V. Puzanov, J. Mol. Struct. 459 (1999) 95.
[45] D.L. Baulch, W.H. Breckenridge, Trans. Faraday Soc. 62 (1966) 2768.
[46] A.S. Averyanov, Y. Khait, G. Ross, Opt. Spekt. 78 (1995) 895.
[47] A.S. Averyanov, Y.G. Khait, Y.V. Puzanov, THEOCHEM 367 (1996) 87.
[48] A.S. Averyanov, Y.G. Khait, Y.V. Puzanov, THEOCHEM 459 (1999) 95.
[49] J. Song, Y.G. Khait, M.R. Hoffmann, J. Phys. Chem. A 103 (1999) 521.
[50] B.M. Elliott, A.I. Boldyrev, J. Phys. Chem. A 109 (2005) 3722.
[51] C.S. Jamieson, C.J. Bennett, A.M. Mebel, R.I. Kaiser, ApJ 624 (2005) 436.
[52] C.S. Jamieson, R.I. Kaiser, Chem. Phys. Lett. 440 (2007) 98.
[53] C.S. Jamieson, A.M. Mebel, R.I. Kaiser, Phys. Chem. Chem. Phys. 7 (2005) 4089.
[54] C.J. Bennett, R.I. Kaiser, ApJ 635 (2005) 1362.
[55] A.M. Mebel, M. Hayashi, V.V. Kislov, S.H. Lin, J. Phys. Chem. A 108 (2004) 7983.
[56] (a) A.P. Scott, L. Radom, J. Phys. Chem. 100 (1996) 16502;
(b) J.P. Merrick, D. Moran, L. Radom, J. Phys. Chem. A 111 (2007) 11683.
[57] G. Rauhut, P. Pulay, J. Phys. Chem. 99 (1995) 3093.
[58] M.P. Andersson, P. Uvdal, J. Phys. Chem. A 109 (2005) 2937.
[59] M.E. Jacox, J. Mol. Spectrosc. 113 (1985) 286.
[60] C.J. Bennett, C. Jamieson, A.M. Mebel, R.I. Kaiser, Phys. Chem. Chem. Phys. 6 (2004) 735.
[61] T. Shimanouchi, J. Phys. Chem. Ref. Data 6 (1972) 993.
[62] C.S. Jamieson, A.M. Mebel, R.I. Kaiser, Chem. Phys. Chem. 7 (2006) 2508.
[63] C.S. Jamieson, A.M. Mebel, R.I. Kaiser, Chem. Phys. Lett. 440 (2007) 105.
[64] C.S. Jamieson, A.M. Mebel, R.I. Kaiser, Chem. Phys. Lett. 443 (2007) 49.
[65] C.S. Jamieson, A.M. Mebel, R.I. Kaiser, Chem. Phys. Lett. 450 (2007) 312.
[66] Y. Ge, K. Olsen, R.I. Kaiser, J.D. Head, Am. Inst. Phys. (2006).
[67] V.J. Barone, Chem. Phys. 122 (2005) 014108.
[68] (a) J.M. Bowman, Acc. Chem. Res. 19 (1986) 202;
(b) R.B. Gerber, M.A. Ratner, Adv. Chem. Phys. 70 (1988) 97;
(c) S. Carter, J.M. Bowman, N.C. Handy, Theor. Chem. Acc. 100 (1998) 191.

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